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RESEARCH IN ENERGETIC COMPOUNDS

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January 1983

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By

K. Baum and T. G. Archibald

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Reaction parameters for the polymerization of 3-azidooxetane, catalyzed by boron trifluoride, were investigated. No significant improvements over the previously attained yields (about 50%) resulted from variations of temperature, catalyst level, water content or the use of 1,4-butanediol as a cocatalyst. Increasing the monomer concentration from 20% to 50%, however, gave 80-90% yields of polymer.

2-Aminoadamantane, prepared from 2-adamantanone and sodium cyanoborohydride, was oxidized to give 2-nitroadamantane. The reaction of 4-bromo-2,2-dinitroadamantane with sodium azide gave 4-azido-2-adamantanone. Nitration of 2,4-adamantanedione dioxime gave the internal nitroso dimer of 2,4-dinitro-2,4-dinitrosoadamantane. Reaction of 2,6-adamantanedione dioxime with NBS gave 2,6-dibromo-2,6-dinitroadamantane. Debromination with sodium borohydride, followed by nitration with tetranitromethane, gave 2,2,6,6-tetranitroadamantane. The reaction of bicyclo[3.3.1]nona-2,6-dione dioxime with hypochlorous acid gave a chlorohydrocarbon, but reaction of the dioxime with chlorine gave 2,6-dichloro-2,6-dinitrosobicyclo[3.3.1]nonane. This nitroso compound reacted with hypochlorous acid to give 2,6-dichloro-2,6-dinitrobicyclo[3.3.1]nonane. 2,6-Diaminobicyclo[3.3.1]nonane, obtained from bicyclo[3.3.1]nona-2,6-dione and sodium cyanoborohydride was oxidized to the 2,6-dinitro derivative.

Synthesis work related to 3-azidooxetane and 3,3-dinitrooxetane is summarized as a journal manuscript.

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I. INTRODUCTION

This report summarizes the research under Contract N00014-78-C-0147 during the period 1 January 1982 through 31 December 1982. Additional work was carried out in the area of energetic oxetanes, with emphasis on a study of reaction parameters for the polymerization of 3-azidooxetane. Work was continued on the synthesis of polycyclic compounds, with the objective of developing procedures for the introduction of multiple energetic groups. A journal manuscript summarizing work on the synthesis of 3-azidooxetane and 3,3-dinitrooxetane comprises Appendix A of this report.

II. OXETANE CHEMISTRY

A. DISCUSSION

In the previous report¹, a streamlined procedure for the preparation multi-pound quantities of 3-azidooxetane was described. Hydroxy-terminated polymers were obtained from 3-azidooxetane with catalysis by boron trifluoride etherate. A problem with this polymerization was that yields were generally in the 50% range. Also, the polymerization reaction is highly exothermic, making scale-up difficult. Typically, quantities of 10 grams in 20% solutions of methylene chloride would show 20 to 30°C exotherms even with external cooling. These problems were addressed by a systematic study of changes in reaction variables.

Reaction Temperature. The effect of temperature on the course of the polymerization is summarized in Table I. The reaction was essentially complete in about 20 minutes at 0-20°C whereas at -30°C the reaction took 24 to 36 hours. At -62°C no significant polymerization occurred although monomer was slowly consumed. In refluxing methylene chloride, the reaction was very rapid and gave a largely insoluble high molecular weight polymer. At a reaction temperature of -30°C the exotherm was readily controlled, but at the monomer concentration used for this series of experiments, 20%, yields were generally in the 50-60% range.

TABLE I

Effect of Temperature on Yield

Temp. Deg.C	% Oxetane reacted	% Yield polymer	Mol. Wt. (VPO)	Physical state
-62	40	0	-	-
-30	80-90	50	2400	Oil
-10	80+	50-60	2400+	Gum
40+	90+	50-60	3400+	Insol. gum

0.1 Mol 3-azidooxetane, 20% solution in methylene chloride
6 mole % $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyst

Catalyst Level. The effects of varying concentrations of boron trifluoride etherate catalyst under the same reaction temperature and monomer concentration are summarized in Table II. As one would expect, increasing the boron trifluoride catalyst concentration has the effect of speeding up the rate of reaction of the 3-azidooxetane. It was found that when 6 mole % of the catalyst used, 60 to

80% of the monomer was consumed in 20 minutes, whereas with 12 mole % catalyst, 100% of the monomer was consumed in the same period. However the conversion to polymer was the same in both cases. When more than 15 mole % of the catalyst was used, the polymer formed was insoluble.

TABLE II

Effect of Catalyst Concentration on Yield

Mole % catalyst	% Oxetane reacted	% Yield polymer	Mol wt.	Appearance
5-6	60-80	50	2400+	oil
9-10	85+	50	2400+	gum
12	100	50-60	2400+	gum
15	100	70+	3400+	insol gum

0.1 Mol 3-azidooxetane, 20% solution in methylene chloride at 0-10°C, boron trifluoride etherate catalyst

The reaction parameter that was found to have the greatest effect on polymer yield was the concentration of the monomer in the reaction solvent (Table III). Thus, increasing the concentration of 3-azidooxetane in methylene chloride from 20 wt % to 50 wt % improved the polymer yield from 50 to 90% without loss of polymer quality. In order to prevent the formation of high molecular weight insoluble polymer, the temperature must be kept below 25°C. To maintain this temperature limit with ca. 0.1 mole batch reactions, it was necessary to start the reaction at -20°C: the reaction was complete in less than a minute. Under these reaction conditions it was found that very little low molecular weight polymer was produced. Thus the usual fractionation with methylene chloride and hexane resulted

in almost no weight loss, suggesting a relatively narrow molecular weight distribution. In larger scale work, a flow system might be used for temperature control. The functionality of the polymer was found to be two

TABLE III

Effect of Monomer Concentration on Yield

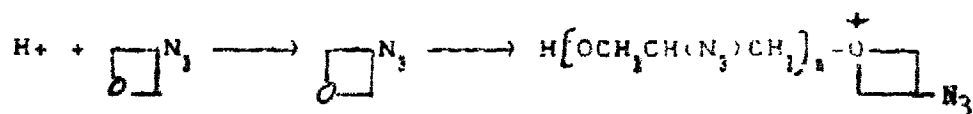
% Monomer by weight	Solvent	% Yield polymer	Mol wt
10	1	50	2400+
20	1	50-60	2400+
50	1	80-90	2400+
12	2	24	<1600
25	2	75	>2000

Solvent: 1, methylene chloride; 2, diethyl ether
Catalyst: 6 mol % boron trifluoride etherate

1,4-Butanediol Cocatalyst. It has been reported¹ that oxetanes are polymerized with a 2:1 complex of boron trifluoride and 1,4-butanediol by stepwise addition of the hydroxy groups to the oxetane rings; polymer yields are almost quantitative, and molecular weights are determined by the amount of initiator. We have applied these conditions to the polymerization of 3-azidooxetane; results are summarized in Table IV. The results are generally similar to those we obtained without 1,4-butanediol. In Table V, parallel experiments at three temperatures are described in which identical conditions were used with and without 1,4-butanediol. It is particularly noteworthy that

in almost all cases no incorporated 1,4-butanediol was detected in the polymers by NMR: in only one case a trace was found.

The generally³ accepted mechanism for the polymerization of an oxetane by a Lewis acid-alcohol complex is based on the liberation of protons from the complex. Protonation of the ring oxygen gives an oxetanonium ion which undergoes a chain reaction with other oxetane molecules:



Insertion of the alcohol into the oxetane ring in the initiation step would not be expected. It is generally thought that the incorporation of alcohols into oxetane polymers takes place in the termination step⁴. Experiments were therefore conducted in which the polymerization reactions were quenched with 1,4-butanediol and with methanol. In these reactions there also was no incorporation of the alcohol into the polymers. This result suggests that termination of polymer growth takes place before quenching by some type of elimination or chain transfer mechanism.

Table IV

Boron Trifluoride and 1,4-Butanediol (BDO) Catalysis

Run	Temp Deg C	Mol % BF ₃ (a)	Mol % BDO (a)	Moles Oxetane	Yield	Mol Wt	BDO Incorp
A	-30	6	3	0.4	30(b)	1300	No
B	-30	6	3	0.4	30(b)	1600	No
C	-30	6	3	0.4	45(b)	2100	No
D	-30	6	3	0.4	51(b)	--	No
E	-30	6	3	0.4	52(b)	1550	No
F	-30	6	3	0.4	52(b)	2400	No
G	-30	6	3	0.4	48(c)	2400	No
H	-15	12	4	0.05	44(c)	2400	No
I	-15	12	5	0.05	12(c)	--	No
J	-15	9	4	0.05	10(c)	2350	Trace
K	2	6	3	0.05	40(c)	2350	No
L	2	9	3	0.05	60(c)	300	No
M	2	12	3	0.05	50(c)	3000+	No

25% Solution of 3-azidooxetane in methylene chloride.

(a) Based on moles 3-azidooxetane. (b) Precipitated from 1:1 methanol-water. (c) Precipitated from 1:1 hexane-methylene chloride.

Table V

Parallel Runs

Run	Temp Deg C	Mol % BF ₃ (a)	Mol % BDO (a)	Moles Oxetane	Yield	Mol Wt	BDO Incorp
A	-30	6	3	0.4	37	2400	No
B	-30	6	0	0.4	48	2400	No
C	-15	6	3	0.5	44	--	No
D	-15	6	0	0.5	36	--	No
E	-2	6	3	0.5	40	2350	No
F	-2	6	0	0.5	55	3000	No

25% Solution of 3-azidooxetane in methylene chloride used; product precipitated from 1:1 hexane-methylene chloride.

(a) Based on moles 3-azidooxetane

Fractional Precipitation. In our earlier work¹, we used fractional precipitation from 1:1 hexane-methylene chloride to remove low molecular weight materials from the

~~3-azidooxetane polymer.~~ Another solvent system that has been used is 1:1 methanol-water.¹ These methods are compared in Table VI, using two polymer mixtures prepared with the butanediol-boron trifluoride catalyst. It is seen that the methanol-water method provides substantially greater yields but the product is of lower molecular weight than the hexane-methylene chloride product. Results similar to those of the methanol-water precipitation were obtained by simple water washing. The physical appearance of the polymer was influenced by small amounts of diluents. Untreated or methanol-water precipitated polymer was a mobile oil, whereas material with a molecular weight of 2,400-3,000 that was precipitated from hexane-methylene chloride and dried thoroughly was a gum. Small amounts of remaining solvent, as little as 5% methylene chloride or monomer, provided fluidity.

TABLE VI

Fractionational Precipitation of Polymers

Run	<u>Methanol-water</u>		<u>Hexane-methylene Chloride</u>	
	% Yield	Mol Wt	% Yield	Mol Wt
A	30	1300	18	2400
B	52	1550	37	2400

0.4 mol 3-azidooxetane; catalyst: 0.024 mol boron trifluoride etherate, 0.012 mol 1,4-butanediol.				

Effect of Water.

Although precautions were always observed to exclude water from the system, the possibility was considered that trace amounts of water would have a detrimental effect on the course of the reaction. It was found, however (Table VII) that reactions run with scrupulously dried equipment and solvents gave the same results as those run in open flasks with untreated industrial grade methylene chloride. Even in the presence of stoichiometric amounts of water, the overall conversion to polymer remained about the same with only a reduction in molecular weight. Even when the reaction was done in equal volumes of methylene chloride and water, some polymer formed.

TABLE VII

Effect of Water

Solvent treatment	% Yield polymer	Mol wt
Dried/ mol sieve	50-60	2400+
None, 0.2% water	55	2400+
1 mol/monomer added	16	2000+
	76	800+

0.1 Mole 3-azidooxetane, 20% solution in methylene chloride
6% mol % boron trifluoride etherate catalyst, 0-10°C

Nitrogen Formation.

It was noted that the polymerization reaction was not improved by incremental additions of catalyst. In general, a catalyst level of 6 mole % was sufficient to consume only about 80% of the monomer. If more catalyst was then added, the remainder of

the monomer disappeared, but no further polymer was formed, and in fact, nitrogen gas began to evolve. The conditions causing the gas formation were investigated (Table VIII). It was found that in reactions kept at 5°C and below, the gas evolution was never more than 3 mol % based on monomer. However, if additional catalyst was added, a mole of nitrogen was liberated for each additional mole of catalyst. In reactions conducted at room temperature, no gas was observed during the course of the polymerization, but when the polymerization was complete, gas evolution began. In reactions containing only boron trifluoride etherate catalyst, 11 mole % nitrogen was observed, whereas when 1,4-butanediol was present, 22 mole % nitrogen was observed. Samples of the polymer yielded no observable gas under the polymerization conditions. When 3-azidooxetane was treated with aqueous sulfuric acid, 22 mole % nitrogen was observed.

Table VIII

Nitrogen Formation

Catalyst	Time (Hrs)	Mol% Nitrogen
A	1	3
A	24	11
B	1	7
B	24	14
C	24	22
D	24	21

A = 6 Mol% boron trifluoride etherate
 B = 12 Mol% boron trifluoride etherate
 C = 6 Mol% boron trifluoride etherate
 + 3 mol% 1,4-butanediol
 D = 50% Aqueous sulfuric acid

Conclusions. The effects of temperature, concentration, catalyst levels, water contamination and alcohol cocatalysts on the polymerization of 3-azidooxetane were studied with the objective of improving polymer yields and controlling the reaction exotherm. The only significant improvement in yield was attained by using higher monomer concentrations than those that were used previously. Under these conditions, batch operation results in a more severe exotherm problem. However, the reaction is so rapid that a continuous flow system would be feasible, and the exotherm could be controlled by regulating the introduction of reagents.

B. EXPERIMENTAL

Polymerization of 3-Azidooxetane (-30 to +40°C). A 50 mL magnetically stirred round bottom flask, fitted with a condenser and drying tube, was loaded with 20 g of a 42% by weight solution of 3-azidooxetane in methylene chloride (0.085 mol). The solution was cooled to -30°C and 0.60 mL (0.0052 mol) of freshly distilled boron trifluoride etherate was added rapidly by syringe. After about 30 seconds the reaction temperature increased to the reflux temperature and a gelatinous polymer formed. The material was allowed to stand for 5 minutes at room temperature and then 5 mL of water was added and the mixture was agitated to disperse the gel. Ethyl acetate (30 mL) was added and

the mixture was stirred for 1 h. The organic layer was separated and dried over magnesium sulfate. Solvent was removed with a rotary evaporator (70°C at 20 mm Hg) to give a brown oil: NMR (CDCl_3) δ 3.58 (s); IR (CH_2Cl_2) 3000, 2900 (CH), 2150 (N_3), 1135 cm^{-1} (C-O-C); molecular weight (vapor pressure osmometry, ethyl acetate) 2200; equivalent weight (silylation) 1200.

The polymer was dissolved in 20 mL of methylene chloride and this solution was poured into 20 mL of hexane with vigorous stirring. After 30 min the solvent was decanted from the precipitated oil, and the product was dried at 70°C under vacuum to give 7.4 g of material essentially identical with the unfractionated polymer.

Polymerization of 3-Azidooxetane (-30°C). A solution of 1.0 g (0.009 mol) of boron trifluoride etherate in 50 mL dry methylene chloride was cooled to -30°C and a solution of 9.9 g (0.1 mol) of 3-azidooxetane in 50 mL of methylene chloride was added dropwise. The solution was stirred at -30. GLC analysis after 6 hours showed that approximately half of the monomer was consumed. The solution was stirred for an additional 48 h period. GLC analysis showed that monomer consumption was 95% complete and essentially no additional monomer monomer was consumed after this time. Saturated sodium chloride solution (5 mL) was added and the mixture was stirred for 30 min. The organic layer was allowed to come to ambient temperature and was washed with 100 mL of 5% potassium carbonate solution and 100 mL water. The methylene chloride solution was dried over magnesium

sulfate and was evaporated under vacuum. The residue was redissolved in 30 mL of methylene chloride and the solution was filtered into 30 mL of rapidly stirring hexane.

After 30 min the solvent was decanted and the remaining oil was washed with 30 mL of hexane. The product was dried at 70°C under vacuum to yield 4.8 g (49%) of a very viscous oil with molecular weight 2350 (VPO, ethyl acetate).

Polymerization of 3-Azidooketane (-30°C, 1,4-Butanediol). Boron trifluoride etherate (3.83 g, 0.027 mol) was added to a solution of 1.25 g (0.0135 mol) of freshly distilled 1,4-butanediol in 50 mL of methylene chloride. This solution was stirred at 25 °C for 1 hour and was cooled to -25°C. Then 3-azidooketane (40.0 g, 0.404 mol) in 150 mL of methylene chloride was added dropwise and the solution was stirred at -30°C for 48 h. The reaction mixture was worked up as above to yield 21.0 g (52%) of viscous oil with molecular weight of 1650 (VPO, ethyl acetate). NMR (DCCl_3) showed no proton absorption between δ 1.5 and δ 2.0 (the central methylene of 1,4-butanediol and its ethers appears at δ 1.6).

In multiple parallel 0.05 mol runs, after 48 hours at -30°C, the polymerization was quenched with 5 mL D_2O , with 5 ml of 1,4-butanediol, with 5 ml of methanol and finally warmed to 25 °C for 15 minutes before quenching with saturated sodium chloride solution. In none of these cases could 1,4-butanediol or methanol be detected in the final polymer.

Nitrogen Evolution Studies. A dry one neck flask, fitted with a gas burette and pressure equalizing bulb, was loaded with a solution of 5.0 g (0.05 mol) of 3-azidooxetane in 20 mL of methylene chloride, and was cooled to 2°C. Then boron trifluoride etherate, (0.3 mL, 0.0026 mol) was added and the evolved gas was measured every 5 min for the first hour and every 15 min thereafter. The concentration of monomer was followed by GLC, using methylene chloride as the internal reference.

2-Azido-1,3-propanediol. To a solution of 100 mL of 10% aqueous hydrochloric acid was added 20 g (0.2 mol) of 3-azidooxetane and the mixture was stirred for 1 h at 25°C. The solution became homogeneous. The product was extracted with two 50 mL portions of methylene chloride and the organic layer was dried over magnesium chloride. Removal of the methylene chloride under vacuum gave 14.0 g, (54%) of a liquid identified as 2-azido-1,3-propanediol: IR (neat) 3400 (O-H), 2950, 2900 (C-H), 2140 cm^{-1} (N_3); NMR δ 3.65 (s). Silylation gave an 18:5 ratio for trimethylsilyl to methylene protons. This material was unstable above 110°C under 0.1 mm Hg. Retreating 3.0 g of this material with 10 mL of 10% aqueous hydrochloric acid for 1 hr gave no methylene chloride extractable materials.

Hydrolytic Stability of Poly-3-azidooxetane. Poly-3-azidooxetane (0.912 g, equivalent weight 1550) was dissolved in 20 mL of methylene chloride and 20 mL of water added. The mixture was stirred rapidly for 4 h. Saturated sodium chloride solution was added and the

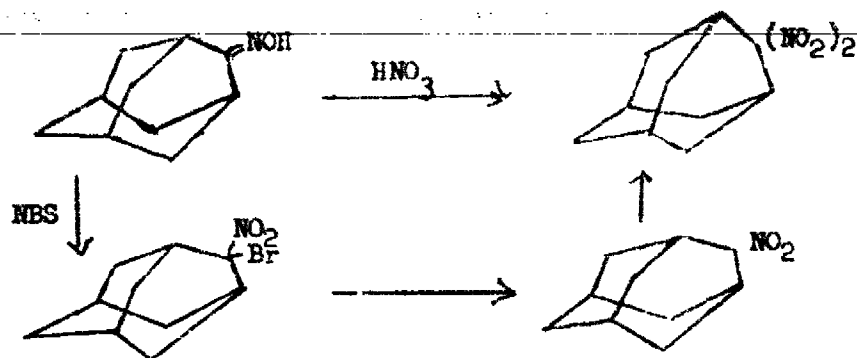
phases were allowed to separate overnight. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated to yield poly-3-azidooxetane (0.902 g, equivalent weight 1500).

In a parallel run, 20 mL of 10% aqueous hydrochloric acid was substituted for water. The recovery of poly-3-azidooxetane was 90% (equivalent weight 1200).

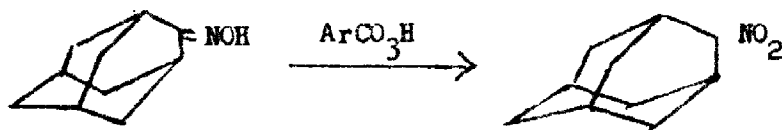
III. POLYCYCLIC NITRO COMPOUNDS

A. DISCUSSION

A study of the synthesis of polycyclic nitro compounds was initiated in the preceding year¹ with the objective of producing useful high density explosives. Monosubstituted adamantanes were used as model compounds for developing methods to introduce gem-dinitro groups into cage molecules. One method used for the preparation of gem-dinitro adamantanes was the direct nitration of the corresponding oximes. In another approach, 2-adamantanone oxime was treated with N-bromosuccinimide or with sodium hypochlorite to give 2-bromo-2-nitroadamantane and 2-chloro-2-nitroadamantane respectively. The bromo derivative was dehalogenated with sodium borohydride, and the resulting 2-nitroadamantane was converted to 2,2-dinitroadamantane by oxidative nitration or by reaction with tetranitromethane.

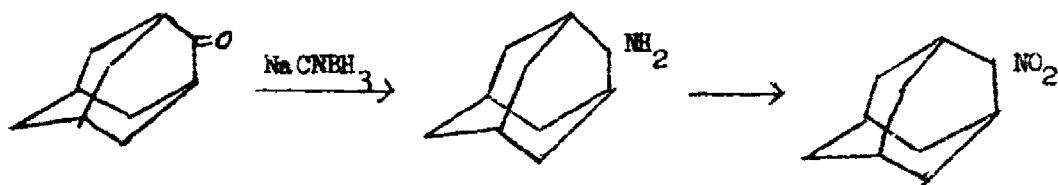


Monofunctional Adamantanes. Work was continued with monofunctional model compounds in order to increase the available options for application to more energetic systems. The direct oxidation of 2-oximinoadamantane to 2-nitroadamantane was attempted with a wide variety of oxidizing agents including manganese dioxide, chromic acid-pyridine, and peracids. The inorganic reagents did not produce 2-nitroadamantane. It was found, however, that relatively strong aromatic peracids gave low yields of the desired product. Thus, *p*-chloroperbenzoic acid in refluxing dichloroethane gave yields below 10% and the use of buffers was ineffective. The major product in this reaction was the ring expanded lactone resulting from the Bayer Villiger oxidation of 2-adamantanone. Attempts to extend this reaction to difunctional oximes were unsuccessful.

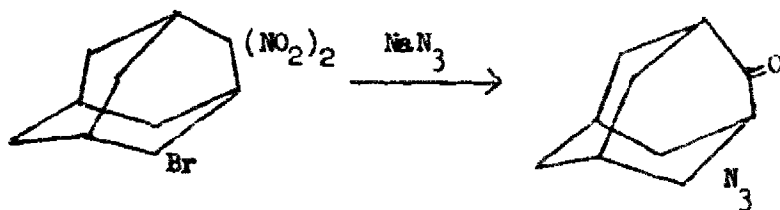


The oxidation of aminoadamantanes is another potential route to nitroadamantanes, inasmuch as there are several

available routes to the amines. The direct conversion of ketones to secondary amines with sodium cyanoborohydride has been reported⁵. We obtained 2-aminoadamantane in 50% yield by the reaction of 2-adamantanone with sodium cyanoborohydride. Conversion of 2-aminoadamantane to the 2-nitro derivative took place in 66% yield with p-nitroperbenzoic acid in refluxing 1,2-dichloroethane.



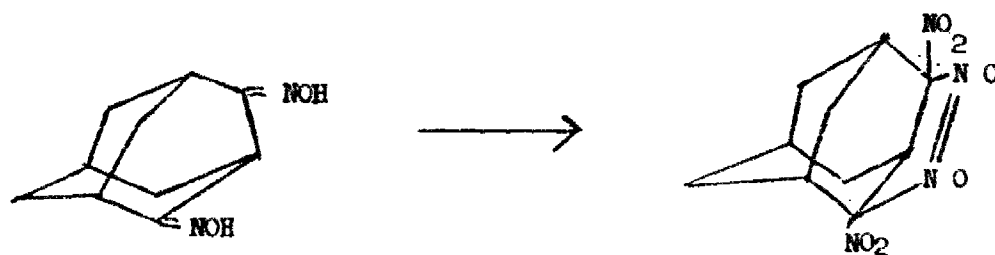
2,4-Derivatives of Adamantane. The ready availability of 4-bromo-2-adamantanone by the treatment of adamantanone oxime with hydrobromic acid⁶, led us to investigate its use as an intermediate to nitroadamantanes. Previously¹, 4-bromo-2,2-dinitroadamantane was obtained from 4-bromo-2-adamantanone by nitration of the oxime. However, attempts to displace the bromine of 4-bromo-2,2-dinitroadamantane with sodium azide at the relatively high temperatures needed for reaction to take place resulted in loss of the nitro groups. 4-Azido-2-adamantanone was isolated.



Previously¹ we reported that the nitration of 2,6-adam-

antanedione dioxime (prepared according to Morat and Rassat⁷) gave a compound that gave elemental analysis data consistent with a dinitrodinitroso derivative. Subsequently, we obtained this same product from 2,4-adamantanedione dioxime, but not from 2,6-adamantanedione dioxime obtained by a different route⁸. It is concluded that the original starting material was the 2,4 derivative, which yields on nitration, 2,4-dinitro-2,4-dinitrosoadamantane. This compound gives a geometrically favored internal nitroso dimer which is not possible for the 2,6 isomer.

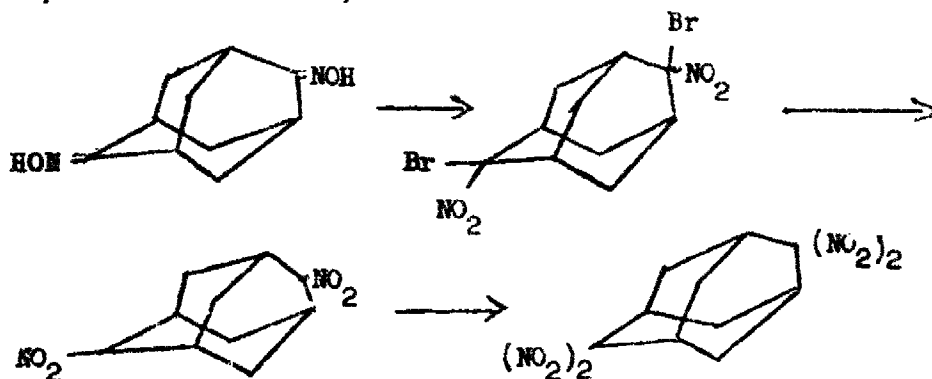
Attempts to convert the nitroso material to 2,2,4,4-tetranitroadamantane under more forcing conditions were unsuccessful. No nitro compounds or nitroso dimers were formed in the reaction of N-bromosuccinimide with 2,4-adamantanedione dioxime.



2.6 Derivatives of Adamantane. There are three reports of 2,6-adamantanedione in the literature. One involves an impractical multi-step synthesis¹, the second a very low yield enamine reaction¹ and the third proved to have an incorrect product assignment⁷. It was reported that 2,6-adamantane dione was obtained in 30% yield by the direct chromic acid oxidation of 2-adamantanone. Reinvestigation showed that this reaction gives

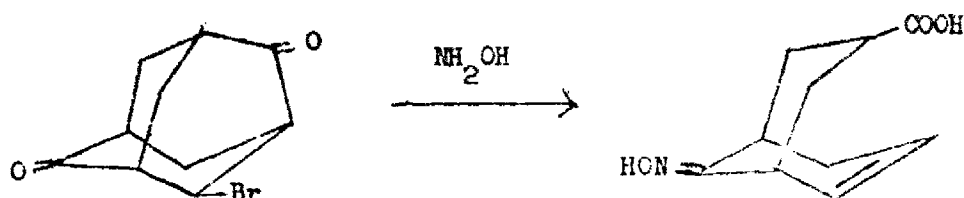
5-acetoxy-2-adamantane and 2,4-adamantanedione with no detectable 2,6-isomer by GLC analysis

The most reasonable route to 2,6-adamantanedione involved a critical dieneamine reaction with methylene iodide which proved to be unreliable and gave poor yields at best. However, sufficient 2,6-adamantanedione dioxime was prepared by this route for a preliminary investigation of its conversion to nitro derivatives. Reaction with N-bromosuccinimide gave 2,6-dibromo-2,6-dinitroadamantane. Subsequently, reduction with sodium borohydride gave 2,6-dinitroadamantane, an intermediate that was not isolated. The crude material was treated with sodium carbonate and tetranitromethane to give a low yield of 2,2,6,6-tetranitroadamantane. The material was identified by elemental analysis, NMR and IR. Its density was 1.75.

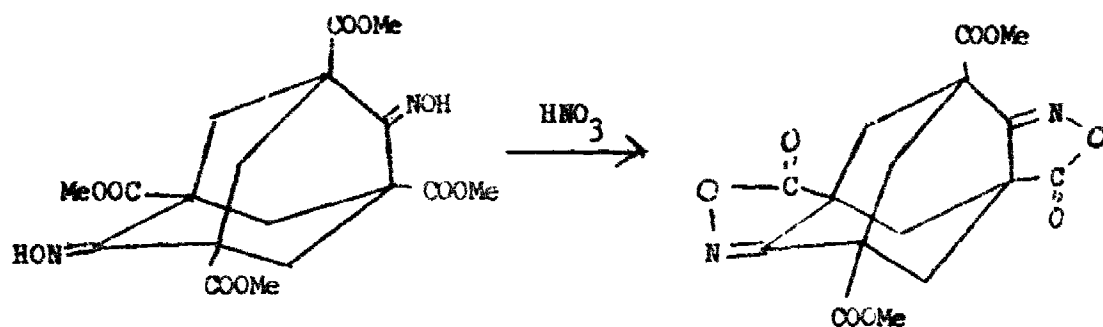


Direct oxidation of 2,6-adamantanedione dioxime with peracids failed to yield nitro compounds. Direct nitration of the oxime gave some conversion to gem-dinitro material, but considerable amounts of ketone were regenerated. However, treating the mixture with hydroxylamine to recycle the carbonyl-containing materials destroyed the nitro compounds present.

~~4-Bromo-2,6-adamantandione¹⁰~~ is more readily accessible than the unsubstituted dione. However, treatment of the material with hydroxylamine gave an 80% yield of 3-carboxy-9-oximinobicyclo[3.3.1]nonene-6.



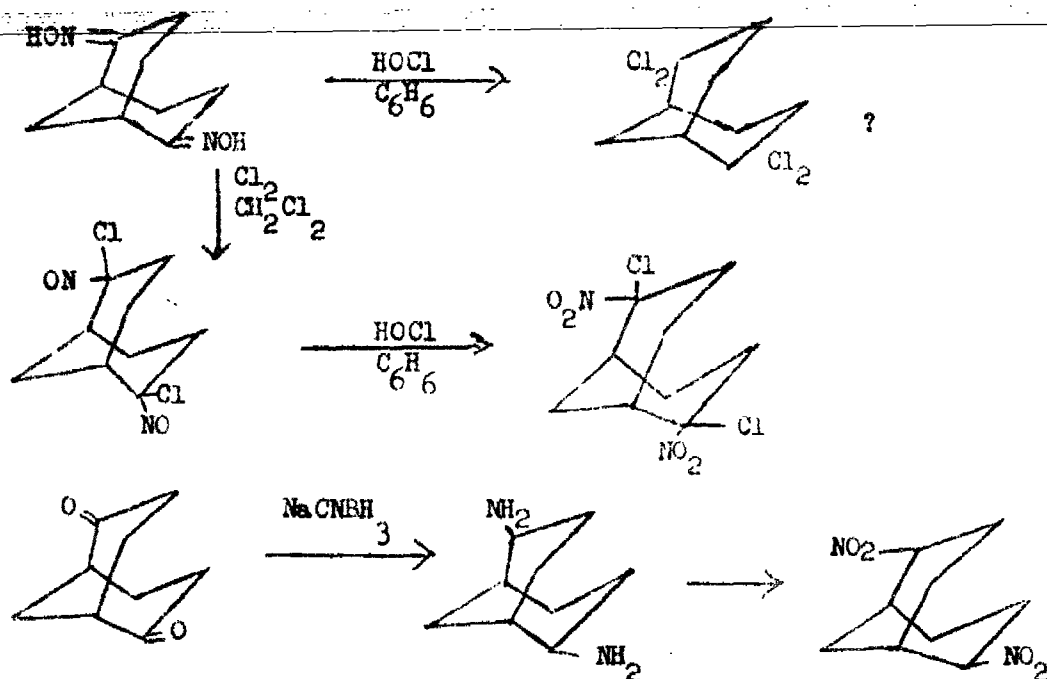
The readily available¹¹ 1,3,5,7-(tetracarbomethoxy)-adamantan-2,6-dione was converted to its dioxime. Nitration or bromination of this material gave no nitro-containing compounds, but rather, ring closure to the isoxatoline took place. This material was observed previously when the oxime was heated with refluxing ethanol¹².



Bicyclo[3.3.1]nona-2,6-dione Derivatives. Because of the difficulty in preparing large quantities of 2,6-adamantanedione, a model system with structural similarities was sought for the development of reaction procedures. Bicyclo[3.3.1]nona-2,6-dione, known as Meerwein's ketone¹³ was selected since it has the same geometry and ring structure with the exception that one of the rings is open.

A general method has recently been reported for the conversion of ketoximes to chloronitro compounds¹⁴; a benzene solution of the oxime is simply treated with neutralized hypochlorous acid in the presence of tetrabutylammonium bisulfate. The dioxime of Meerwein's ketone reacted under these mild conditions to give a high yield of a chlorohydrocarbon; no nitrogen or oxygen remained. Further work is needed to assign the structure. The appearance of a transient blue coloration suggested that a nitroso intermediate was involved. Subsequently, the oxime was treated with elemental chlorine in methylene chloride. Under these conditions, the nitroso compound was formed as evidenced by a persistent blue color of the solution. Removal of the methylene chloride and addition of the material to the benzene-hypochlorous acid reagent then gave a 59% yield of the expected chloronitro derivative of Meerwein's ketone, 2,6-dichloro-2,6-dinitrobicyclo[3.3.1]nonane.

Direct reduction of the dioxime to the diamine with lithium aluminum hydride failed, but the diamine was prepared directly from Meerwein's ketone with sodium cyanoborohydride. Oxidation of this diamine with p-nitroperbenzoic acid gave the 2,6-dinitro derivative, and conversion of this compound to the tetranitro derivative is being studied.



B EXPERIMENTAL

Peracid Oxidation of 2-Adamantanone oxime. To a refluxing solution of 10.0 g of 85% p-chloroperbenzoic acid in 50 mL of 1,2-dichloroethane was added, portionwise, 1.65 g (0.010 mol) of 2-adamantanone oxime. A slight green color was observed. After a 3 h reflux period, the solution was cooled, filtered, washed with 20 mL of 5% sodium carbonate and evaporated to yield 1.5 g of a waxy solid. IR and NMR analysis showed 0.15 g (8.3%) of 2-nitroadamantane and 1.3 g (81%) of 3-oxahomoadamantan-2-one. Attempts to improve this ratio by running the reaction in the presence of disodium hydrogen phosphate in acetonitrile reduced the yield of 2-nitroadamantane to a trace.

2-Aminoadamantane. A mixture of 100 mL of anhydrous methanol, 25 g of ammonium acetate and 5.0 g (0.033 mol) of 2-adamantanone was stirred for 1 h at room temperature.

Then 3.0 g (0.049 mol) of sodium cyanoborohydride was added and the solution was stirred for 24 h. The solution was acidified with concentrated hydrochloric acid to pH 2 and was extracted twice with 50 mL of ether. Evaporation of the ether yielded 2.1 g (42%) of 2-hydroxyadamantane. The water solution was then made alkaline with solid potassium hydroxide to pH >10. Water was added to prevent crystallization of potassium chloride. The solution was extracted with methylene chloride (2x50 mL). The organic layer was dried over magnesium sulfate and the solvent was removed to yield 2.52 g (50%) of 2-aminoadamantane, m.p. 180-185°C, identified by comparison with an authentic sample.

Peracid Oxidation of 2-Aminoadamantane. To a solution of 5.0 g (0.025 mol, 96% assay) of p-nitroperbenzoic acid in 100 mL of refluxing 1,2-dichloroethane was added, dropwise, a solution of 1.0 g (0.0067 mol) 2-aminoadamantane in 25 mL 1,2-dichloroethane. The solution was refluxed for 30 min, cooled and filtered. The solution was extracted with a pH 5.0 phosphate buffer (2x50 mL), dried over magnesium sulfate and evaporated to yield 1.15 g of a semi-solid which upon recrystallization from ethanol-water gave 0.80 g. (66%) of 2-nitroadamantane, identified by IR and NMR comparison with authentic material.

Reaction of 4-Bromo-2,2-dinitroadamantane with Sodium Azide. Sodium azide (0.5 g), activated by recrystallization from water-acetone, was added to a solution of 0.1

g (0.000326 mol) 4-bromo-2,2-dinitroadamantane in 10 mL of dimethyl formamide. The solution was kept at 100 to 120°C for 12 hrs, cooled, and added to 100 mL of water. The organic material was extracted with methylene chloride (2 x 50 mL) and the resulting solution was dried over magnesium sulfate. Evaporation of solvents and sublimation of the residual oil yielded 0.015 g (25%) of 4-azido-adamantan-2-one, identified by IR comparison with authentic material.

2,6-Adamantanedione Dioxime. To a refluxing solution of 1.05 g (0.006 mol) of 2,6-adamantandione in 50 mL of ethanol was added a solution of 4.0 g (0.005 mol) of hydroxylamine hydrochloride and 2.0 g of sodium carbonate in 20 mL of water. The solution was allowed to stand for 48 h and was then concentrated to one third of its original volume. The precipitate was filtered to yield 1.00 g (99%) of 2,6-adamantandione dioxime, mp 279-280°C.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.26; N, 14.41. Found: C, 61.84; H, 7.40; N, 14.19.

2,6-Dibromo-2,6-dinitroadamantane. To a solution of 0.50 g (0.0025 mol) of 2,6-adamantandione dioxime in 50 mL of 1:1 dioxane-water was added 3.0 g (0.018 mol) of N-bromosuccinimide, and 1.5 g (0.017 mol) of sodium bicarbonate, and the mixture was stirred at ambient temperature for 48 h. The color initially turned light green then slowly faded. The dioxane was evaporated under vacuum and 50 mL of water added. The solid product was recrystallized from ethanol-water to give 0.23 g (24%) of

2,6-dibromo-2,6-dinitroadamantane. mp 160-165°C. IR (CH₂Cl₂) 3000 (C-H), 1540 1460 cm⁻¹ (N-O); NMR (DCCl₂) δ 1.8 - 2.8 complex.

Anal. Calcd for C₁₀H₁₂N₂O₂Br₂: C, 31.27; H, 3.15; N, 7.29; Br, 41.26. Found: C, 31.33; H, 3.14; N, 7.45; Br, 41.44.

2,2,6,6-Tetranitroadamantane and 6,6-Dinitro-2-adamantanone. To a solution of 0.31 g (0.00008 mol) of 2,6-dibromo-2,6-dinitroadamantane in 20 mL of ethanol was added 0.1 g of sodium borohydride and 10 mL of water. The solution was stirred at 25°C for 30 min. The ethanol was evaporated under vacuum and the aqueous solution was extracted with ether (2 x 50 mL). The ether solution was dried over magnesium sulfate and evaporated to yield crude 2,6-dinitroadamantane a waxy solid, mp 140-150°C (NMR δ 4.4 2 protons, δ 1.8-2.7 12 protons). The nitro compound was dissolved in a solution of this material in 10 mL of methanol was stirred with a solution of 0.2 g of sodium carbonate in 10 mL of water for 15 min at 20°C. Tetranitromethane (1.0 mL) was added and the mixture was stirred for 1 h. The methanol was evaporated, 20 mL of water was added, and the product was extracted with ether (2 x 50 mL). The ether layer was washed with 50 mL of 5% sodium carbonate solution and 50 mL of 10% potassium hydroxide solution, dried with magnesium sulfate and evaporated to yield 0.16 g of crude solid, mp 150-200°C. TLC of this material on silica gel with chloroform yielded 0.040 g, (20%) of 6,6-dinitro-2-adamantanone: IR (CH₂Cl₂)

3000 (C-H), 1720 (C=O), 1580 and 1460 cm^{-1} (N-O), NMR (DCCl_3) δ 3.7 (2 H), 2.7 (2 H) and 2.4 ppm (8 H).

Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_3$: C, 50.01; H, 5.03; N, 11.60. Found: C, 50.26; H, 5.07; N, 10.74.

A second TLC band with slightly less retention time provided 0.010 g (2.4%) of 2,2,6,6-tetranitroadamantane. The material sublimed without melting above 280°C: IR (CH_2Cl_2) 3000 (C-H), 1580 and 1460 cm^{-1} (N-O); NMR (DCCl_3) δ 3.4 (4 H) and 2.0 ppm (8 H); density, 1.75.

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{N}_4\text{O}_8$: C, 37.96; H, 3.82; N, 17.72. Found: C, 39.93; H, 4.13; N, 16.80.

Reaction of 4-Bromo-2,6-adamantanedione with Hydroxylamine. A solution of 1.0 g (0.0041 mol) of 4-bromo-2,6-adamantanedione, 1.0 g (0.014 mol) of hydroxylamine hydrochloride and 1.0 mL of pyridine in 35 mL of absolute ethanol was refluxed for 2 h. The solvent was then evaporated, 50 mL of water was added and the mixture was stirred for 30 min. The water was decanted and the oil was recrystallized from ethanol to give 0.65 g (80%) of 3-carboxy-9-oximinobicyclo[3.3.1]nonan-6-ene, mp 285°C (dec). This product was identical with material obtained by oximation of 4-bromo-2,6-adamantanedione in ethanol-water or oximation of 3-carboxy-9-oxobicyclo[3.3.1]nonan-6-ene directly. No dioxime could be detected.

2,6-Dibromo-2,6-dinitrobicyclo[3.3.1]nonane.

N-Bromosuccinimide (10.0 g, 0.056 mol) was added, with stirring at 5°C, to a solution of 1.50 g (0.008 mol) of

bicyclo[3.3.1]nona-2,6-dione dioxime (mp 215-217°C) in 100 mL of water and 150 mL of dioxane. Then 5.0 g of solid sodium bicarbonate was added over a 20 min period. The solution became green and then blue and the color faded in 30 min. The mixture was stirred 30 min at 5°C and 2 hrs at ambient temperature. The reaction mixture was concentrated to one third of its original volume with a rotary evaporator under reduced pressure and was extracted with two 100 mL portions of methylene chloride. The organic layer was separated and dried over magnesium sulfate. Flash column chromatography of the resulting oil (silica gel, methylene chloride) yielded a nitro containing fraction (IR) and several fractions containing only carbonyl compounds. Recrystallization of the nitro containing oil from ethanol-water yielded 0.20 g (6.5%) of pure 2,6-dibromo-2,6-dinitro bicyclo[3.3.1]nonane, mp 143-144°C; IR (KBr) 2950 (C-H), 1540, 1450 cm^{-1} (N-O); NMR (DCCl_3) δ 2.0-3.0 (complex).

Anal. Calcd for $\text{C}_9\text{H}_{11}\text{N}_2\text{O}_4\text{Br}_2$: C, 29.06; H, 3.25; N, 7.53; Br, 42.96. Found: C, 29.20; H, 3.33; N, 7.36; Br, 43.12.

Reaction of Bicyclo[3.3.1]nona-2,6-dione dioxime with Hypochlorous Acid A pH meter was used to neutralize 200 mL of commercial pool bleach (5% sodium hypochlorite) to pH 5.0 at 0-2°C with 10% sulfuric acid. Benzene (100 mL) and 5.0 g (0.027 mol) of bicyclo[3.3.1]nona-2,6-dione dioxime were added. As the dioxime dissolved, the solution became deep blue and then the color slowly faded. After 1 h, 100

ml of unneutralized bleach and 0.5 g of tetra-n-butylammonium bisulfate were added and the mixture was stirred for an additional 2 hours. The organic layer was separated, washed with 5% sodium thiosulfate solution and dried with magnesium sulfate. The benzene was evaporated and the residual oil was dissolved in hexane and filtered thru 5 g of silica gel. Evaporation of the hexane gave an oil which solidified to give 4.2 g of a waxy solid, mp 18-22°C: IR (CH_2Cl_2) 3000 (C-H), 1440, 1460 cm^{-1} (C-Cl); NMR (DCCl_2) δ 2.0-2.8.

Anal. Found: C, 43.09; H, 5.86; Cl, 51.15.

2,6-Dichloro-2,6-dinitro-bicyclo[3.3.1]nonane.

Chlorine gas was bubbled into a solution of 2.0 g (0.011 mol) of bicyclo[3.3.1]nona-2,6-dione dioxime in 50 mL of methylene chloride. The dioxime slowly dissolved and the solution became dark blue and then green. This solution was stirred for 4 h and the methylene chloride was removed. Then, 50 mL of benzene 0.2 g of tetra-n-butylammonium bisulfate and 50 mL of 5% sodium hypochlorite were added and the solution was stirred for 48 h. The organic layer (now colorless) was separated, washed with 5% sodium thiosulfate and dried over magnesium sulfate. The benzene was evaporated and the residual oil was dissolved in 50 mL of methylene chloride and was filtered through 5 g of silica gel. The methylene chloride was evaporated and the residual semi-solid was recrystallized from ethanol to yield 1.84 g (59%) of 2,6-dichloro-2,6-dinitro-bicyclo[3.3.1]nonane, mp 111-113°C: IR (CH_2Cl_2) 3.000

(CH), 1,580 and 1,460 cm^{-1} (N-O); NMR (DCCl_3) δ 2.0-3.0.

Anal. Calcd for $\text{C}_9\text{H}_{11}\text{Cl}_2\text{N}_2\text{O}_4$: C, 38.18; H, 4.27; N, 9.89; Cl, 25.04. Found: C, 38.28; H, 4.21; N, 8.79; Cl, 26.31.

2,6-Diamino-bicyclo[3.3.1]nonane. A mixture of 100 mL of anhydrous methanol, 30 g of ammonium acetate and 10.0 g (0.066 mol) of bicyclo[3.3.1]nona-2,6-dione was stirred at 20°C for 2 h. Then 6.0 g (0.1 mol) of sodium cyanoborohydride was added slowly over 1 h. A water bath was used to keep the temperature of the exothermic reaction at 20°C. The mixture was stirred 24 h, the methanol was evaporated under vacuum and the pH was adjusted to below 2 with concentrated hydrochloric acid. The solution was extracted with ether (2 X 50 mL). The aqueous layer was then made basic (pH 13) with solid potassium hydroxide; water was added as necessary to prevent salt precipitation. The solution was cooled and was extracted with methylene chloride (2 X 50 mL). The organic layer was dried over magnesium sulfate and the solvent was removed to yield 6.2 g (61%) of 2,6-diamino-bicyclo[3.3.1]nonane as a oil. IR (CH_2Cl_2) 3400-3300 (N-H), 2900 (C-H), 1450, 1320, 1270, 1110, 960 cm^{-1} ; NMR (DCCl_3) δ 2.0-3.5; P-nitrobenzoate, mp. 190-192°C. Elemental analysis results are pending.

Oxidation of 2,6-Diaminobicyclo[3.3.1]nonane. A solution of 5.0 g (0.032 mol) of 2,6-diamino-bicyclo[3.3.1]nonane in 100 mL of 1,2-dichloroethane was heated to reflux. Then 25 g (80% purity, 0.1 mol) of p-nitroperbenzoic acid was added slowly over a 30 min

period. The mixture was refluxed for 3 h, cooled and filtered. The solution was washed with pH 5.0 buffer (2 x 30 mL), dried over magnesium sulfate and stripped of solvent to yield 1.50 g (21%) of crude 2,6-dinitrobicyclo(3.3.1)nonane as an oil: IR (CH_2Cl_2) 3000 (C-H), 1550 and 1460 cm^{-1} (N-O); NMR (DCCl_3) δ 4.2 (2 H) and 1.8-3.0 (12 H). Upon attempted distillation this material decomposed. On passing the material through silica gel, all nitro functions were lost.

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Synthesis of Electron-Deficient Oxetanes.

3-Azidooxetane, 3-Nitrooxetane and

3,3-Dinitrooxetane¹.

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ABSTRACT

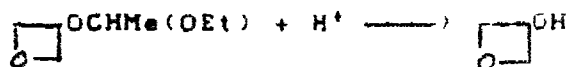
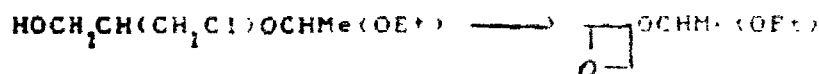
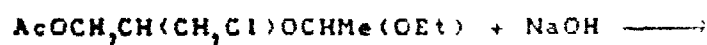
A facile synthesis of 3-hydroxyoxetane is described, based on the addition of acetic acid to epichlorohydrin, protection of the resulting primary alcohol as an acetal, basic acetate hydrolysis and ring closure, and removal of the protecting group. 3-Azidooxetane was prepared from 3-tosyloxyoxetane and sodium azide. Reduction of the azide with triphenylphosphine or hydrogen gave 3-aminooxetane, and oxidation of the amine with m-chloroperbenzoic acid gave 3-nitrooxetane. Oxidative nitration or reaction with tetranitromethane gave 3,3-dinitrooxetane. 3-Azidooxetane and 3,3-dinitrooxetane were polymerized with Lewis acids

Recently we reported the synthesis of 3-fluoro-3-nitrooxetane by the base-catalyzed ring closure of the monotriflate derived from 2-fluoro-2-nitro-1,3-propanediol². The "fluorine effect", or the destabilization of a nitronate salt by an adjacent fluorine, enables this ring closure to take place despite the general tendency of 2-nitro alcohols to split off formaldehyde (reverse Henry reaction). The use of a less potent leaving group, such as tosylate, gave adducts of 1-fluoro-1-nitroethylene rather than the oxetane³, and even triflates from nonfluorinated nitroalcohols such as 2,2-dinitro-1,3-propanediol and 2-(hydroxymethyl)-2-nitro-1,3-propanediol gave no oxetanes¹.

An alternative to this ring closure is the introduction of nitro groups by operating on oxetanes which contain other reactive functional groups. The conversion in high yield of 3-hydroxyoxetane to the tosylate has been reported, and the tosylate group has been displaced by halides⁴. The 3-hydroxyoxetane was obtained by the hydrolysis of 3-propenoxyoxetane, which, in turn, was prepared by the base-catalyzed rearrangement of 3-allyloxyoxetane. The latter compound, however, was obtained only in low yield by the cyclization of 2-allyloxy-3-chloropropanol⁵, a low-conversion chlorination product of allyl alcohol^{5,6}.

We have developed a procedure suitable for the preparation of large quantities of 3-hydroxyoxetane from

epichlorohydrin using the route outlined in Scheme 1. The hydroxyl group of the acetic acid adduct of epichlorohydrin was blocked with a base-resistant protecting group. Ester hydrolysis and ring closure with aqueous base was followed by deblocking with acid.



Scheme 1.

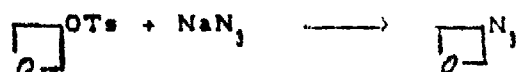
The reaction of epichlorohydrin with acetic acid, catalyzed by ferric chloride, has been reported to give 3-chloro-2-hydroxy-1-propyl acetate in high yield⁷. This procedure was modified by eliminating the use of solvents and minimizing the amount of catalyst. The low iron level did not prevent monitoring the reaction by NMR, and the product was used without workup for the following step. The hydroxyl group was then protected with a vinyllic ether⁸. Dihydropyran and ethyl vinyl ether gave similar results, and p-toluenesulfonic acid was used as a catalyst. No solvent was used and to this point, we have none yet

process. Next, aqueous sodium hydroxide hydrolyzed the ester and also closed the oxetane ring. The resulting crude 3-(1-ethoxyethoxy)oxetane was then treated with methanol and a catalytic amount of p-toluenesulfonic acid to give 3-hydroxyoxetane. Flash distillation gave 3-hydroxyoxetane of about 80% purity, and the pure alcohol could be isolated by fractionation. The impure material, however, was suitable for conversion to the tosylate with aqueous sodium hydroxide and tosyl chloride⁴. The overall yield of 3-tosyloxyoxetane based on epichlorohydrin was 29%.

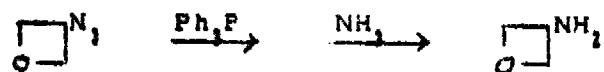
Attempts to prepare 3-nitrooxetane from 3-tosyloxyoxetane, 3-bromooxetane or 3-iodooxetane by displacement reactions with silver nitrite or sodium nitrite were unsuccessful. Decomposition took place when reaction temperatures were high enough for the consumption of starting materials. It has been reported⁴ that displacements of 3-tosyloxyoxetane with metal halides require temperatures of about 170°C and that the reaction of 3-iodooxetane with diethylamine takes place at 200°C.

Azide salts, however, were found to react with 3-tosyloxyoxetane under relatively mild conditions to give 3-azidooxetane. A 50% yield was obtained with potassium azide at 87°C in hexamethylphosphoramide and a 28% yield was obtained in refluxing acetonitrile in the presence of 18-crown-6. Polyethylene glycols were also reported to have crown-ether type complexing ability⁵, and these materials were investigated as solvents for the displacement. Sodium

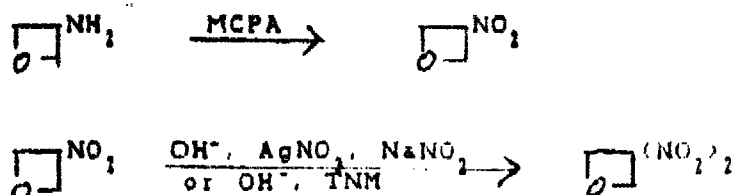
azide and the tosylate gave an 86% yield of 3-azidooxetane at 120-130°C at 7-10 mm Hg; under these conditions, the product was distilled from the reaction mixture as it was formed. The solvent did not codistill with the product when tetraethylene glycol or higher homologs were used. The azide was handled safely¹⁰ by distilling the material directly into methylene chloride and using the solution for subsequent reactions.



3-Aminooxetane was obtained in low yield from the reaction of 3-tosyloxyoxetane with liquid ammonia. A more satisfactory method, however, was the reduction of 3-azidooxetane. Azides have been converted to amines by a reaction with triphenylphosphine followed by ammonolysis¹¹, and by this procedure, 3-azidooxetane gave a 96% yield of 3-aminooxetane. This reduction was also carried out by hydrogenation at atmospheric pressure in methanol over 10% palladium on carbon, but the reaction was not reliably reproducible. The synthesis of 3-aminooxetane by the high pressure hydrogenation of 3-oxetanone oxime has been reported in the patent literature¹².

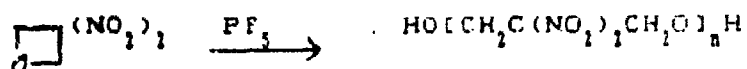


3-Aminooxetane was used as a starting material to prepare 3-nitrooxetane and 3,3-dinitrooxetane. The oxidation of cyclohexylamine with *m*-chloroperbenzoic acid to give nitrocyclohexane has recently been reported¹³. This reaction was found to give a 75% yield of 3-nitrooxetane from 3-aminooxetane. The most generally used method for converting a mononitro aliphatic compound to a gem-dinitro compound is the oxidative nitration reaction¹⁴, using base, sodium nitrite and silver nitrate. 3,3-Dinitrooxetane was obtained in this way from 3-nitrooxetane but only in 22% yield. Nitronate salts have recently been nitrated with tetranitromethane¹⁵. Addition of this reagent to a solution of the salt of 3-nitrooxetane in aqueous methanol gave a 60% yield of 3,3-dinitrooxetane.

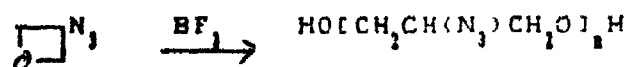


The polymerization of 3-fluoro-3-nitrooxetane was previously shown to be catalyzed by the strong Lewis acid catalyst, phosphorus pentafluoride, but not by boron trifluoride. 3,3-Dinitrooxetane was found to be even more resistant to cationic polymerization, requiring prolonged exposure to an atmosphere of phosphorus pentafluoride. A

polymer was obtained with a melting point of 200-202°C. The polymer was insoluble in methylene chloride or ethyl acetate, but was soluble in acetone. The molecular weight by vapor pressure osmometry was 2870.



3-Azidooxetane, which is not so highly deactivated by electron-withdrawing groups, was polymerized readily by boron trifluoride etherate, at temperatures as low as -30°C. Details are described in the Experimental Section.



Determination of the hydroxyl equivalent weight of polymers has generally provided difficulties¹⁶. We have used a simple procedure consisting of trimethylsilylation, removal of volatiles, and determination of silyl hydrogens by quantitative NMR.

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. A Varian 920 gas chromatograph was used for

GLC separations, and a Mechrolab 301A vapor pressure osmometer was used for molecular weight determinations.

3-Toxvloxvioxetane. Epichlorohydrin (925 g, 10.0 mol) was added with stirring, over a 10 min period, to a solution of 1.5 g of ferric chloride in 612 g (10.02 mol) of glacial acetic acid. The mixture was heated at 65-70°C for 24 h to give crude 3-chloro-2-hydroxy-1-propyl acetate; NMR (CDCl_3) 2.10 (s, 3 H, COCH_3), 3.80 (m, 6 H, $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$); IR (film) 3500 (OH), 1735 cm^{-1} (COCH_3).

After 10 g of p-toluenesulfonic acid monohydrate was added to this crude material, 815 g (11.3 mol) of ethyl vinyl ether was added dropwise, with stirring, over a period of 2 h. The flask was cooled to maintain a reaction temperature of 35-37°C. After the addition was completed, the mixture was heated at 35-40°C for 16 h to give crude 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate.

This intermediate was added over a 1.5 h period with stirring to a solution of 1.1 kg (27.5 mol) of sodium hydroxide in 1.1 L of water at 105°C, and the reaction mixture was refluxed for an additional 4 h period. The mixture was cooled and was washed with 1.5 L of water. The aqueous layer was washed with 1.5 L of methylene chloride, and the combined organic phases were stripped of solvent to give 1.2 kg of crude 3-(1-ethoxyethoxy)oxetane.

Methanol (400 g) was added and the mixture was cooled to 15-18°C. p-Toluenesulfonic acid monohydrate (10 g) was added with stirring. The reaction temperature increased

over a 5 min period to 34°C and then decreased to 20°C in 30 min. The mixture was stirred for an additional 45 min period and then 5 g of solid sodium bicarbonate was added. Distillation gave 280 g of 3-hydroxyoxetane, bp 45-50°C (0.3 mm), of 80% purity (NMR).

This 3-hydroxyoxetane (3.07 mol) was stirred with 660 g (3.46 mol) of technical p-toluenesulfonyl chloride in 530 mL of water, and a solution of 194 g (4.84 mol) of sodium hydroxide in 200 mL of water was added over a period of 25 min. Ice bath cooling was used to keep the reaction temperature below 70°C. When the exothermic reaction subsided, the bath was removed and the mixture was allowed to cool to 40°C over a 1 hr period. The product was isolated by filtration, washed with four 180 mL of warm (50°C) water, and air dried to give 649 g (93%) of 3-tosyloxyoxetane, mp 86-88°C (reported¹ 88.5-89°C).

3-Azidooxetane. A stirred solution of 92 g (0.40 mol) of 3-tosyloxyoxetane and 40 g (0.48 mol) of sodium azide in 205 mL of polyethylene oxide (Carbowax 300) was heated to 120-130°C over 30 min at 7-10 mm Hg. The product distilled as it was formed, over a 1.5 h period, and was collected in a stirred receiver containing 200 mL of methylene chloride at -78°C. The resulting methylene chloride solution contained 34 g (86%) of 3-azidooxetane, and an analytical sample was isolated by GC (9% QF-1 on Chromasorb W, 100°): ¹H NMR (CDCl₃) δ 4.70 (m, 4 H, CH₂), 4.76 (m, 1 H, CHN₃), IR (CH₂Cl₂) 3000, 2930 (CH), 2150 (N₃), 880 cm⁻¹ (oxetane).

Anal. Calcd for $C_7H_7N_3O$. C, 36.36; H, 5.09; N, 42.41.
Found: C, 36.29; H, 4.82; N, 43.06.

The product was handled safely as a methylene chloride solution (see discussion)

3-Aminooxetane. Triphenylphosphine (132.5 g, 0.50 mol) was added to a solution of 50 g (0.50 mol) of 3-azidooxetane in 800 mL of methylene chloride at 0-5°C. The solution was allowed to stand for 0.5 h at 0-5°C and for 3.5 h at room temperature. The solvent was removed under vacuum, and an ice-cooled solution of 800 mL of methanol saturated with ammonia was added to the residue. The resulting orange solution was stirred for 40 h at 0-5°C. Distillation gave 32 g of 3-aminooxetane, bp 50-82°C (60-70 mm Hg) - reported¹¹ 80-82°C (100 mm Hg) - and extraction of the distillation residue with ether followed by distillation gave an additional 3.2 g (96% total): ¹H NMR (CDCl₃) δ 2.03 (s, 2 H, NH₂), 4.0-4.8 (m, 5 H); IR (film) 3350 (NH₂), 3000, 2900 (CH), 1605 (NH₂), 970 cm⁻¹ (oxetane); n_D²⁰ 1.4500. Elemental analysis was carried out on the p-nitrobenzamide, mp 189-191°C.

Anal. Calcd for $C_{10}H_{10}N_2O_3$. C, 54.03; H, 4.50; N, 12.60. Found: C, 54.02; H, 4.51; N, 12.32

3-Nitrooxetane. A solution of 7.0 g (0.10 mol) of 3-aminooxetane in 100 mL of 1,2-dichloroethane was added over 1 hr to a refluxing solution of 71 g (0.35 mol) of 85% m-chloroperoxybenzoic acid in 600 mL of 1,2-dichloroethane. The reaction mixture was heated at reflux for an additional

3 h period and was allowed to stand at ambient temperature for 16 h. The precipitated m-chlorobenzoic acid was filtered and was washed with 1,2-dichloroethane. The combined solutions were stripped of solvent under vacuum and the residue was distilled in a Kugelrohr apparatus to give 6.35 g (62%) of 3-nitrooxetane at 27°C (0.5-1.0 mm Hg). An analytical sample was isolated by GC (9% QF-1 on Chromosorb W, 120°C): NMR (CDCl_3) δ 4.87 (m, 4 H, CH_2), 5.23 (m, 1 H, CHNO_2), IR (CH_2Cl_2) 3000, 2940 (CH), 1550, 1370 (NO_2), 980 cm^{-1} (oxetane); n_D^{20} 1.4618; d 1.33.

Anal. Calcd for $\text{C}_3\text{H}_5\text{NO}_2$: C, 34.96; H, 4.89. Found: C, 34.77; H, 4.87.

3,3-Dinitrooxetane (Oxidative Nitration) A solution of 3.38 g (0.033 mol) of 3-nitrooxetane, 1.45 g (0.036 mol) of sodium hydroxide and 2.56 g (0.036 mol) of sodium nitrite in 72 mL of water at 0-5°C was added to a stirred solution of 12.2 g (0.072 mol) of silver nitrate in 25 mL of water at 0-5°C. An immediate black suspension formed. After the reaction mixture was stirred at 0-5°C for 2 h, 20 mL of saturated sodium chloride solution was added and stirring was continued for 30 min. The mixture was filtered through celite and the filter cake was washed with 10 mL of water and 100 mL of ether. The aqueous solution was washed with two 100 mL portions of ether and the combined ether solutions were dried and the solvent was removed. Column chromatography of the residue (silica gel, methylene chloride-hexane) gave 1.07 g (21.9%) of

Appendix A

3,3-dinitrooxetane, mp 70-71°C (subl 100°C); NMR (CDCl_3) δ 5.27 (s); IR (CH_2Cl_2) 3000, 2940 (CH), 1580, 1325 (NO_2), 1000 cm^{-1} (oxetane); d, 1.65.

Anal. Calcd for $\text{C}_3\text{H}_4\text{N}_2\text{O}_5$: C, 24.34; H, 2.72. Found: C, 24.54; H, 2.80.

3,3-Dinitrooxetane (from Tetranitromethane). A solution of 1.03 g (0.010 mol) of 3-nitrooxetane and 2.0 g (0.010 mol) of tetranitromethane in 5 mL of methanol was added dropwise, with stirring over a 20 min period, to a solution of 0.42 g (0.010 mol) of sodium hydroxide in 1 mL of water and 2 mL of methanol at 0°C. Stirring was continued for 30 min and 10 mL of water was then added. The pH was adjusted to 9-10 with sodium hydroxide, and the mixture was extracted with ether (3 x 25 mL). The ether solution was washed with water and dried. Removal of the solvent gave 0.89 g (60%) of 3,3-dinitrooxetane identical with that above.

Polymerization of 3,3-Dinitrooxetane. A dry 100 mL flask, fitted with a syringe valve, was loaded with a solution of 0.113 g (0.76 mmol) of 3,3-dinitrooxetane in 0.5 mL of dry methylene chloride, and was flushed with 21% of a white solid: MW (VPO, ethyl acetate) 484; IR 3530 (OH), 1575, 132 of phosphorus pentafluoride was added. After 30 h, solvent and catalyst were removed under vacuum. Extraction of the residue with 15 mL of methylene gave 0.018 g (16%) of recovered 3,3-dinitrooxetane. The material insoluble in methylene chloride was extracted with

15 mL of ethyl acetate to give 0.024 g (21%) of a white solid: MW (VPO, ethyl acetate) 484; IR 3550 (OH), 1575, 1320 cm^{-1} (NO_2). The material insoluble in ethyl acetate was extracted with 15 mL of acetone to give 0.071 g (63%) of white solid, mp 200-202°C: NMR (D_2CCOCD_3) δ 4.67 (br s); IR (acetone) 3600 (OH), 1565, 1320 cm^{-1} (NO_2); molecular weight (vapor pressure osmometry, acetone) 2670; density 1.59.

Polymerization of 3-Azidooxetane. A 50 mL magnetically stirred round bottom flask, fitted with a condenser and a drying tube, was loaded with 20 g of a 42% by weight solution of 3-azidooxetane in methylene chloride (0.085 mol), and was cooled to -30°C . Freshly distilled boron trifluoride etherate (0.60 mL, 0.0052 mol) was added rapidly by syringe. After about 30 sec the reaction temperature increased to the reflux temperature and a gelatinous polymer formed. The material was allowed to stand for 5 min at room temperature and then 5 mL of water was added and the mixture was agitated to disperse the gel. Ethyl acetate (30 mL) was added and the mixture was stirred for 1 h. The organic layer was separated and was dried over magnesium sulfate. Solvent was removed with a rotary evaporator (70°C at 20 mm Hg) to give a brown oil: NMR (CDCl_3) δ 3.58 (s); IR (CH_2Cl_2) 3,000, 2900 (CH), 2150 (N_3), 1135 cm^{-1} (C-O-C); molecular weight (vapor pressure osmometry, ethyl acetate) 2200; equivalent weight (silylation) 1200.

Appendix A

The polymer dissolved in 20 mL of methylene chloride was poured into 20 mL of hexane with vigorous stirring. After 30 min the solvent was decanted from the precipitated oil, and the latter was dried at 70°C under vacuum to give 7.4 g of material essentially identical with the unfractionated polymer.

The polymerization was also carried out at subambient temperatures with more dilute solutions. A solution of 1.0 g (0.0071 mol) of boron trifluoride etherate in 50 mL of methylene chloride was cooled to -30°C and a solution of 9.9 g (0.10 mol) of 3-azidoxyetane in 100 mL of methylene chloride was added dropwise. The solution was stirred at -30°C for 48 h. GLC analysis showed that less than 0.5% of the oxetane remained. Saturated sodium chloride solution (5 mL) was added and the mixture was stirred for 30 min. The organic layer was allowed to come to ambient temperature and was washed with 100 mL of 5% potassium carbonate solution and with 100 mL of water. The methylene chloride solution was dried over magnesium sulfate and was evaporated under vacuum. The residue was dissolved in 30 mL of methylene chloride and the solution was filtered into 30 mL of rapidly stirred hexane. After 30 min the solvent was decanted and the remaining oil was washed with 30 mL of hexane. The product was dried at 70°C under vacuum to yield 4.8 g (49%) of very viscous oil with molecular weight 2350 (VPO, ethyl acetate).

A similar reaction using 0.1 mol of 3-azidoxyetane

and 0.0052 mol of boron trifluoride etherate in 50 mL of methylene chloride, maintained at 0-5°C gave a 54.5% yield of product with a molecular weight of 2400

Equivalent Weight Determination. A 50 mL round bottom flask wquiped with a magnetic stirrer, a condenser and a drying tube was loaded with approximately 0.2 g of 3-azidooxetane polymer, 5 mL of 1,2-dichloroethane, 2 mL of 1,1,1,3,3,3-hexamethyldisilazane and 0.5 mL of chlorotrimethylsilane. Volatile materials were removed at 70°C under vacuum. The residue was dissolved in 1 mL of deuteriochloroform and the proton NMR spectrum was recorded. The hydroxyl equivalent weight was calculated on the basis of the areas of the δ 3.3 signal (5 protons per monomer unit) and the δ 0 signal (9 protons per siloxy group. The same method was used for polymers with more complex NMR spectra by using weighed mixtures of the silylated polymer and a reference such as p-dichlorobenzene. The equivalent weight was calculated on the basis of the areas of the reference and siloxy signals.

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Appendix A

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